CHAPTER-2

ION EXCHANGE EQUILIBRIA

IN

AQUEOUS ACETONE-SUCCINIC ACID MEDIUM

INTRODUCTION

A physical description of the interaction of a counter ion with its surrounding water structure and with the fixed ionic sites within an ion exchange resin is of considerable interest and importance in understanding ionic selectivities of these systems. Gregor's theory[1] postulates that selectivity arises primarily because of differences in the partial volumes of the counter ions which are related to the degree of ionic hydration. Thus, the resin has a higher affinity for the least hydrated ion. Harris and Rice[2,3] have explained ionexhange selectivities in terms of the electrostatic interaction of a counter ion with the fixed ionic site and with the solvent and give, in this sense a more molecular picture of the resin phase system. The counterions are viewed as existing in two states : some are located in the close proximity of the fixed ion, while others are termed as free.

Before the mechanism of ion exchange is considered it is possible to make following fundamental assumptions.

(1) Ion exchange always proceeds by equivalents, that is ion for ion, otherwise electrical neutrality would not be maintained.

(2) An ion exchanger acts as a highly-ionised salt, although, for weak exchangers, the free acid or free basic forms may be only slightly ionised in the resin phase.

(3) The active ions in the exchanger are completely mobile, that is, they mix freely with one another.

The Mechanism of Ion Exchange

The mechanism of ion-exchange reactions have been explained in two ways : (a) from the view point of the law of mass action and (b) in the light of the Donnan hypothesis.

(a) From the view point of the law of mass action

An ion-exchange reaction may be considered as proceeding according to the equation :

$$R\,X^{+} + Y^{+} \rightleftharpoons R\,Y^{+} + X^{+} \qquad \text{-----}\ (1)$$

Where R stands for the non-exchangeable part of the resin, and X^{+} and Y^{+} for the mutually exchangeable ions.

The reaction is reversible, so that, as first approximation, the law of mass action may be applied, and

$$\left[Y_r^{+}\right]\ \left[X_s^{+}\right] = k\ \left[X_r^{+}\right]\ \left[Y_s^{+}\right] \qquad \text{-----}\ (2)$$

The subscripts r and s indicate ions in the resin phase and the external solution respectively, and the square brackets indicate molar concentrations (M). In ion exchange work, it is usual to express concentrations in the resin phase as moles per gram of exchanger, when equation (2) becomes

$$m_y\ (X^{+}s) = k\ m_x\ \ (Y^{+}s) \qquad \text{-----}\ (3)$$

Where m_x and m_y are concentrations of X and Y in moles per gram of exchanger. It is found that this equation is not exact, and various empirical equations have been suggested in place of it, one of the most useful of these is that of Rothmund and Kornfeld [4] derived from the Freundlich adsorption isotherm. The equation is

$$\frac{m_Y}{m_X} = K \left[\frac{(Y^{+}\ s)}{(X^{+}\ s)} \right]^{p} \qquad \text{-----} \ (4)$$

If log $\frac{m_Y}{m_X}$ versus log $\frac{(Y^{+}_{\ s})}{(X^{+}_{\ s})}$ is plotted[4] at various concentrations of the solution, the straight lines result at concentrations below 0.1 M.k for any given ion can be extrapolated from the graph. When the external solution is more concentrated than 0.1 M the curves are no longer liner, but flatten out because activity effects come into play.

The most important factors that influence the equilibrium state at higher concentrations are : (1) the combination of two different ions in the resin phase may not always produce a truly - homogeneous solid solution; (2) in general, change of ion is accompani-ed by change of volume of the exchanger; and (3) the affinity of different ions for any one exchanger varies.

<u>From the viewpoint of the Donnan hypothesis</u>

An ion exchanger may be considered as a semi-permeable membrane of inert material containing within it a concentrated solution of elevtroyet. A cation exchanger in the hydrogen form may be considered as corresponding to a solution of acid inside a membrane, the solution is assumed to be completely ionised, as would be the case for a strong exchanger, and the hydrogen ions are free to wander. Some of them will find their way through the membrane, and may even move a short distance away from it, but they will be prevented from moving very far by the electrostatic charges remaining on the anionic part of the exchanger.

If the exchanger is brought into contact with a solution, for example sodium-chloride, an exchange of sodium and hydrogen ions will immediately begin to take place, partly on the surface of the resin and partly by diffusion through the membrane; hence the Donnan hypothesis can be applied. This hypothesis states that the ratios of the activities of two ions is the same on both sides of semi-permeable membrane. Taking hydrogen and sodium as the ions, then

$$a(Na)_{ex} \cdot a(H)_{sol} = a(H)_{ex} \cdot a\,(Na)_{sol} \qquad \text{-----}\ (5)$$

where a stands for activity. Activity is related to the concentration by the equation

$$a = \gamma C \qquad \text{-----}\ (6)$$

where a = activity, C = concentration and γ is the activity coefficient. We will consider two cases namely (1) the solution concentration is less than 0.1 M and (2) the solution concentration is greater than 0. 1 M.

(1) <u>Thesolution concentration is less than 0. 1 M</u>

In this case, the activities of the ions in the solution may be assumed to be equal to their concentrations. Whence from equation (5)

$$\left[\frac{C_{Na}}{C_H} \cdot \frac{\gamma\,Na}{\gamma\,H}\right]_{res} = \left[\frac{C_{Na}}{C_H}\right]_{sol} \qquad \text{-----}\ (7)$$

Or

$$\left[\frac{C_{Na}}{C_H}\right]_{res} = \left[\frac{C_{Na}}{C_H}\right]_{sol} \left[\frac{\gamma\,H}{\gamma\,Na}\right]_{res} \qquad \text{-----}\ (8)$$

As the ionic concentration in the resin phase remains constant, $\left[\frac{\gamma\,H}{\gamma\,Na}\right]_{res}$ may be considered to be constant over a wide range. This ratio is the equilibrium constant of the exchanger for the particular pair of ions considered.

(2) The solution concentration is greater than 0. 1 M

In this case, the activities of the ions in solution can not be assumed to be equal to their concentrations so that equation (5) becomes

$$\left[\frac{C_{Na} \cdot \gamma\,Na}{C_H \cdot \gamma\,H}\right]_{res} = \left[\frac{C_{Na} \cdot \gamma\,Na}{C_H \cdot \gamma\,H}\right]_{sol} \qquad \text{-----}(9)$$

$$\left[\frac{C_{Na}}{C_H}\right]_{res} = \left[\frac{C_{Na}}{C_H}\right]_{Sol} \left[\frac{\gamma\,H}{\gamma\,Na}\right]_{res} \left[\frac{\gamma\,Na}{\gamma\,H}\right]_{sol} \qquad \text{-----}(10)$$

$$K_{Na\text{-}H} = \left[\frac{\gamma\,H}{\gamma\,Na}\right]_{res} \left[\frac{\gamma\,Na}{\gamma\,H}\right]_{Sol} \qquad \text{------}(11)$$

in general, $\left[\frac{\gamma\,Na}{\gamma\,H}\right]_{sol}$ is less than 1 for strong solution, so that the equilibrium constant decreases as the solution becomes more concentrated.

When ions of two different valencies take part in the exchange, the Donnan equation is modified; for example for the system hydrogen-calcium the constants

$$K_{Ca-H} = \left[\frac{\gamma H^2}{\gamma Ca}\right]_{res} \qquad \text{-----} \ (12)$$

for dilute solutions, and

$$K_{Ca-H} = \left[\frac{\gamma H^2}{\gamma Ca}\right]_{res} \left[\frac{\gamma Ca}{\gamma H^2}\right]_{sol} \qquad \text{-----} \ (13)$$

for strong solutions.

EARLIER WORK

Equilibrium exchange reactions were studied in aqeous and mixed organic solvent media. Alkali metal ions have been studied with the cation exchange resins in the NH_4^+ form[5].

The studies on Li^+/H^+, Na^+/H^+, K^+/H^+ exchanges on Amberlite IR-120 and Dowex 50WX8 in ethanol-water and acetone-water were reported by Gupta, Ghate and Shankar[6]. The euqilibrium constants in mixed solvents are found to be related to the corresponding equilibrium constants in aqueous systems through the appropriate solvent activity terms and the mixed solvents. It has been shown that the logarithm of solvent activity terms is linearly related to the logarithm of the electrolyte activity coefficient. This relationship has been found to be independent of the resin and solvent composition, and dependent on the cations being used and the nature of the organic solvent.

Equilibrium quotients have been obtained for exchange in the Na^+/H^+, NH_4^+/H^+ and Ag^+/Na^+ cation systems on Dowex 50 in anhydrous methanol[7]. The ionic strength of the solution was maintained at 0.1 M and exchange was studied as a function of the resin composition.

Cation-exchange studies have been performed for univalent ions in aqueous solutions with a porous sulphonic acid type of exchanger (Amberlite IR-112), a weakly acidic carboxylic type of exchanger (Amberlite-IRC 50) and carbonaceous exchanger (Sulphonated Coal) in hydrogen forms by Bhatnagar and Arora[8].

The linear increase of percentage of exchange was noted with increase of ethanol percentage. It was observed that there is a regular increase of percentage of exchange and increase of $\log_{10}$ Ka. Effect of the quantity of resin and of presence of anions on exchange of cations have also been studied.

Concentration equilibrium quotients i.e. selectivity coefficients have been measured[9] at 30° for the following cation exchange systems and solvents using Dowex 50X8 of alkali metal ions M^+ with H^+ form of the cation exchange resin in methanol-water mixtures. Changes in the degree of ionsolvation and ion pair formation are believed to account for the generally enhanced metal selectivities in alcoholic system.

Equilibrium studies for exchange of univalent cations on Dowex 50X8 in H^+ form have been made[10] in aqueous acetone media. The data has been used to evaluate the thermodynamic equilibrium constant for Li^+/H^+, K^+/H^+, NH_4^+/H^+ and Ag^+/H^+ ions

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in different aqueous acetone solutions. The exchange has been found to increase linearly with increase in percentage of acetone in the mixed solvent. The affinity sequence at lower acetone percentages (upto 30%) was found to be $Li^{+} < Na^{+} < NH_4^{+} < Ag^{+}$; while at higher percentage (50%) silver exchanged positions with NH_4^{+} in this sequence which now becomes the sequence of their naked ionic radii also.

Equilibrium studies for the exchange of bivalent alkaline earth metal ions on Dowex 50WX8 in H^{+} form have been make in aqueous acetone media[11]. The data has been used to evaluate the thermodynamic constants for Mg^{2+}/H^{+}, Ca^{2+}/H^{+}, Sr^{++}/H^{+} and Ba^{2+}/H^{+} exchanges in different aqueous acetone solutions. In cases of Mg^{2+}/H^{+}, Ca^{2+}/H^{+} exchange has been found to decrease linearly with increase in percentage of acetone in the mixed solvent; whereas it increases with acetone percentage for Ba^{2+}/H^{+} exchange. The affinity sequence for alkaline earth metal ions has been found to be $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ both in purely aqueous and aqueous acetone media.

Selectivity coefficients, $K\frac{M}{H}$, for the exchange of alkali metal ions and ammonium with the hydrogen form of Zeokarb 225 cation-exchange resin have been determined[12] in various organic solvent-water and organic solvent-water--phenol mixtures. There is an increase in $K\frac{M}{H}$ in paring from purely aqueous conditions to media of increasing organic solvent content, frequently with the effect of producing magnified differences and selectivity reveals between one ion and another.

Equilibrium studies for exchange of zinc, copper, cobalt and nickel ions on Dowex 50x8 resin in hydrogen form in water-acetone carboxylic acids media were reported by Kulkarni and Jadhav[13]. The equilibrium constants were evaluated and the exchange was found to decrease linearly with increase in acetone content.

PRESENT WORK

It was thought that further studies of equilibria would be interesting from the analytical point of view of separation of mixtures. The results of ion-exchange equilibria of Mn, Hg, Al, Co, Ca and Pb with aqueous-acetone and aqueous acetone-succinic acid for H^+ ions on Dowex 50 W-X8 are presented. The equilibrium constants are computed at 0.004 M metal ions and at various percentages of acetone.

EXPERIMENTAL

Solutions (1) 0.05M solutions of chlorides of Mn, Al, Co, Ca and nitrates of Hg and Pb.

(2) Acetone % - 0, 20, 30, 50.

(3) Succinic acid.

PROCEDURE

The exchange studies were carried out by equilibrating 50 ml of required metal ion solution with 1 g of the H^+ form of the resin Dowex 50W-X8. After equilibration (24 hrs) aliquents (2 ml) were withdrawn from such batches to determine

TABLE 2C,

EQUILIBRIUM EXCHANGE REACTION BETWEEN M^{n+}/H^{+} and $M^{n}(nSA)^{n+}/H^{+}$

Metal Ion	Acetone Percentage	Ka X 10^{-3}		XBR X 10^{-3}	
		a	b	a	b
Mn(II)	0	3.35	3.35	4.60	4.601
	20	2.764	1.638	4.12	4.05
	30	1.85	1.638	5.28	4.05
	50	1.0619	0.952	3.77	3.464
Hg(II)	0	27.5	14.0	14.29	12.78
	20	5.3	4.3	13.2	14.02
	30	3.7	2.5	18.55	20.06
	50	0.055	2.1	19.30	19.50
Al(III)	0	3.454	4.75	2.56	2.73
	20	4.9375	2.15	2.9	2.66
	30	0.3	0.5	1.21	1.24
	50	1.8	1.0	1.21	1.45
Co(II)	30	40.50	12.15	5.96	7.78
	50	10.36	4.05	3.56	5.96
Ca(II)	30	3.05	23.05	3.056	3.45
	50	1.357	14.5	2.85	2.90
Pb(II)	20	8.4	4.201	21.75	21.75
Mg(II)	20	20.0	3.645	5.49	5.56

a = Aqueous acetone.

b = Aqueous acetone + 0.5 M succinic acid.

the extent of exchange. The amount of ions exchanged in the process was determined by titrating aliquots for un-exchanged metal ions, Calcium, Magnesium, Mangenese, Lead, Aluminium and Mercury with disodium EDTA [14]. The apparent equilibrium constant K_a was calculated by using the relation.

$$K_a = \frac{X_{BR}^{2+}}{X_{AR}^{2}} \cdot \frac{C_{AS}^{2}}{C_{BS}^{2+}}$$

Where X terms are equivalent fractions of ions in the resin phase, while C terms are the concentrations of ions in the solution phase.

DISCUSSION

The values of the apparent equilibrium constant Ka for Ca^{2+}/H^{+}, Mg^{2+}/H^{+}, Mn^{2+}/H^{+}, Pb^{2+}/H^{+}, Cd^{2+}/H^{+}, Al^{3+}/H^{+} and Hg^{2+}/H^{+} exchanges in 0, 20, 30 and 50% of acetone and in succinic acid are given in table 2C1.

The equilibrium constant decreases with the increase in percentage of acetone upto 50%. This shows that the exchange varied linearly with the concentration of acetone, and this can be correlated with the dielectric constant of the mixture. The dielectric constants at 0, 10, 30 and 50% are 78.2, 73.0, 61.0 and 48.0 respectively[15], showing that these similarly vary with the concentration of acetone.

Ion-exchange occurs in polar solvents in the similar way as it occurs in water. The process of ion-exchange becomes too complex in non-aqueous and mixed solvents due to the interplay of various and often opposing factors. Equilibrium exchange in such systems depends on the degree of dissociation in the resin and solution phase, ionic solution, swelling pressure, complex-formation and other specific interactions like ion-pair formation and ion-association. Nature of the solvent influences all these phenomena. Acetone, the solvent which has been used in the present studies, mixed with water in varying proportion can hinder the process of ionic disso--ciation for inorganic electrolytes and helps other ionic interactions just like other organic solvents.

Results of this exchange studies presented in tables 2 C_1 show that the equilibrium constant is generally in the order

$Ka\ Hg > Ka\ Ac > Ka\ Mn$ - - - - - - - - - (all % acetone)

$Ka\ Co > Ka\ Hg > Ka\ Al > Ka\ Ca > Ka\ Mn$ (30-50 % acetone)

Zn, Mg, Cu, Ni, Cd, Co, Pb and Th are highly adsorbed on the resin in aqueous acetone and aqueous acetone - SA medium. The exchange reaction of these metal ions with H^+ ions of Dowex 50 W-X8 is fully completed. The equilibrium constant for Mn^{2+} exchange is lower than other metal ions. The equilibrium constant for Ca^{2+} is greater than that for Mg^{2+} ions. The relation between the affinity for the resin and ionic size in the equilibria involving the alkine-earth chlorides is shown by Scatchard and Teffit[16]. The smooth curve of log K -

k versus $1/\overset{\circ}{a}$ indicates that ionic size does play a determining role. This can be so if each bivalent ion in the resin phase is situated close to one of its neutralising sulphonate groups and relatively far from the other. Such a position might well be that of minimum potential energy.

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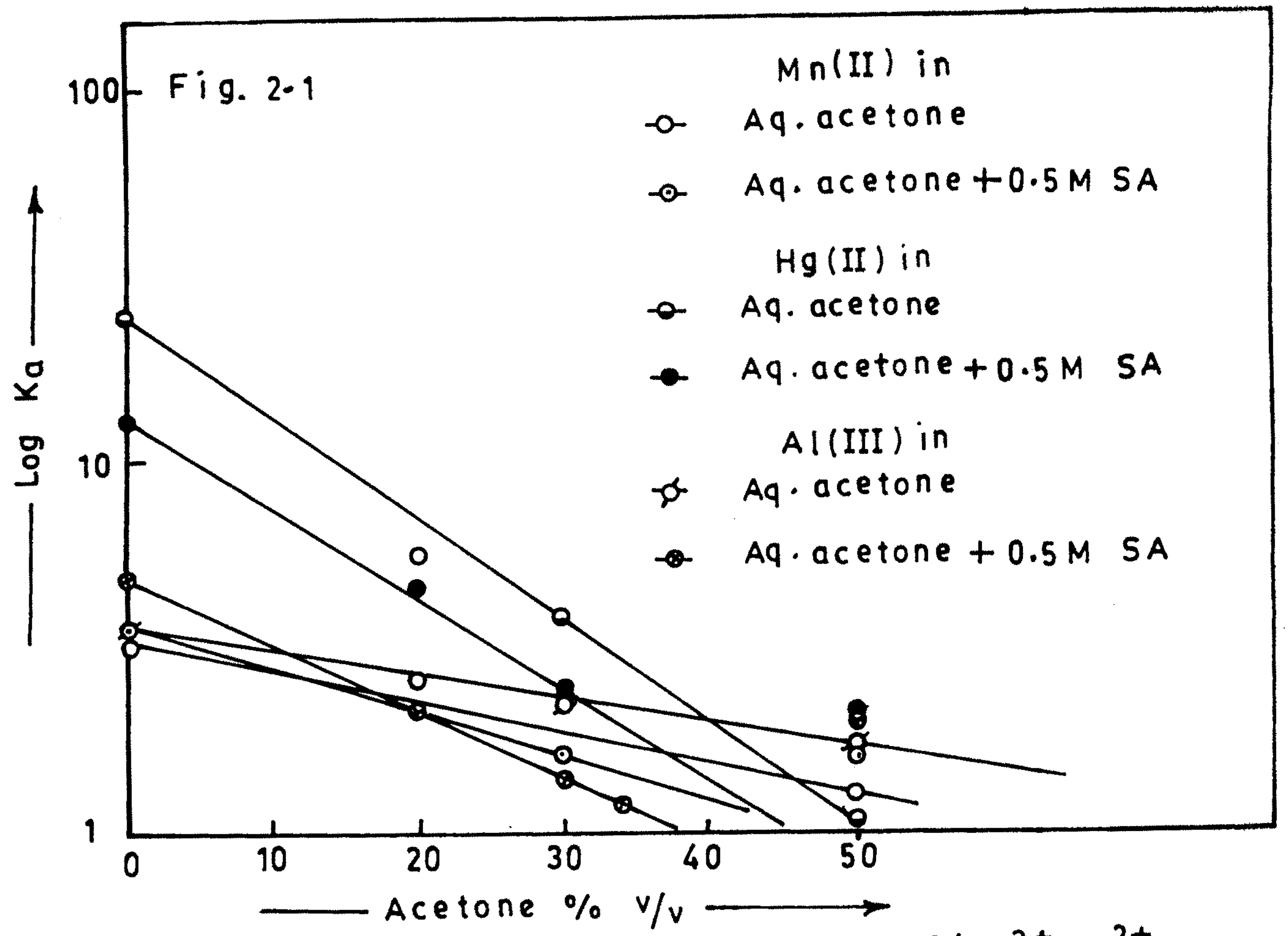
TABLE 1 - 2A

IONIC RADII OF METAL IONS

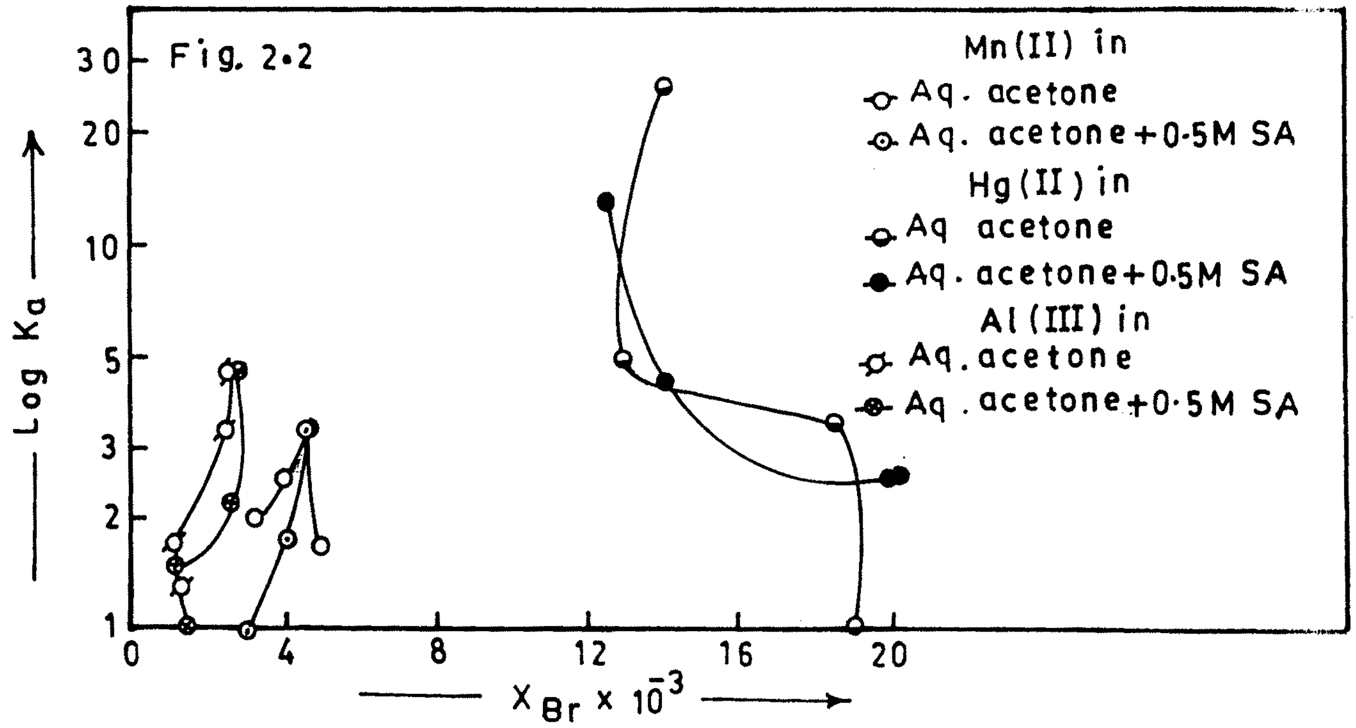
Metal ion	Ionic radii (in A°)	Metal ion	Ionic radii (in A°)
Cu(II)	0.96	Ca(II)	0.99
Zn(II)	0.74	Pb(II)	1.21
Mg(II)	0.65	Th(IV)	0.95
Ni(II)	0.69	Al(III)	0.50
Cd(II)	0.97	Hg(II)	1.1
Co(II)	0.72	Sr(II)	1.13
Mn(II)	0.80	Ba(II)	1.35

The affinity of Pb^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+} and Mn^{2+} ions in the equilibria may be due to ion association[18]. It is exceedingly difficult to say whether ionic size or ion association is the primary determining factor because activity coefficients reflect both degree of dissociation and ionic size. Knowledge of the degree of dissociation can alone enable the true activities in the aqueous phase to be calculated.

The ionic radii of Cd^{2+}, Ca^{2+} and Pb^{2+}, are moreover the same and hence the affinity of these ions towards the



Variation of Log Ka with Acetone % for Mn^{2+}, Al^{3+}, Hg^{2+}, in Aqueous acetone; Aqueous Acetone — 0·5 M SA media.



Variation of Log Ka with X_{Br} at various percentage of acetone for Mn^{2+}, Al^{3+}, Hg^{2+}, in Aqueous acetone; Aq. Acetone — 0·5M SA media.

resin is in the same range. The affinity of M_g^{2+} ions is less than Pb^{2+}, Ca^{2+} and Cd^{2+} ions and the affinity of Mn^{2+} ions is the least as its radii are very small. It can be concluded that the greater the diameter of the ion, the more firmly it is held by the exchanger, which supports the view that affinity is related to the activity coefficient of the ion in the resin phase. A practical value for the comparison of affinities of ions is given by the equilibrium constants. It follows that the greater the affinity an ion for an exchanger, the more difficult it will be to remove the ion by subsequent elution with a solvent. These conclusions are supported by the results of separation of metal ions, presented in chapter four. As managanese ions have smaller ionic radii these are preferentially eluted than other ions under study.

The variability of Ka with X_{BR} has been shown in table 2C1 and fig. 2.2 for aluminium, mercury and manganese, ions under the conditions of present studies. The plots of log Ka with X_{BR} for these ions at different acetone percentages show a regular change in the values of equilibrium coefficients with increase in equiv-alent fraction of the metal ion in the resin phase. There is no regular increase or decrease in the values of Ka with the change in X_{BR}. Thus, in mixed solvents, just like aqueous ones, the trend of Ka variation with X_{BR} is not uniformly similar in all cases. Such irregular variations of Ka with X_{BR} has been shown previously by Duncan and Lister[19] for alkali metal hydrogen exchanges in aqueous media. The same has been shown in nonaqueous and mixed solvents by Bhatnagar for alkali hydrogen exchanges[20] and alkaline earth metal ions hydrogen exchanges by Lowen etal [21] and Reichenberg etal[22]. The similar irregular trend was noticed[13] in Zn^{2+}/H^{+}, Cu^{2+}/H^{+}, Co^{2+}/H^{+} exchanges in water-acetone-carboxylic acid media. The results of the present studies are in line with those obtained by all these earlier workers. The results of the equilibrium studies are helpful in knowing nature of the exchange reaction.

REFERENCES

1 Gregor, H.P., J. Amer. Chem.Soc. 73,642 (1950).

2 Harris, F.E. and Rice, S.A.,
J.Chem. Phys., 24, 1258 (1958).

3 Harris. F.E. and Rice, S.A.,
Z. Physik. Chem. 8, 207 (1956).

4 Rothmund, V. and Kornteld, G.,
Z. Anorg. Chem., 103, 129 (1918), 108,215(1919).

5 Kressman, T.R.C. and Kitchener, J.A.,
J. Chem. Soc., 1211 (1949).

6 Gupta, A.R, Ghate, M.R. and Shankar, J.,
India J. of Chem., 5, 316 (1967).

7 Gable, R.W. and Stroble, H.A.,
J. Phys. Chem.,60, 513 (1956).

8 Bhatnagar, R.P. and Arora, R.C.,
J.Indian Chem. Soc., 42(9), 640 (1965).

9 Fessler, R.G. and Stroble, H.A.,
J.Phys. Chem., 67, 2562 (1963) .

10 Bhatnagar, R.P. and Sharma, S.N.
Journal of Jiwaji University 2, (34) (1974).

11 Bhatnagar, R.P. and Sharma, S.N., Journal of
Jiwaji University, 3, 122 (1975).

12 Jones, J.G. and Thomas, J.D.R.,Talanta 19, 961 (1972)

13 Desai A.V., M.Sc. Thesis, Shivaji University, 1981.

14 Vogel, A.T., "A Text Book of Quantitative Inorganic Analysis", Longmans Green, London, 433, 435, 443 (1961)

15 Timmermans Physico Chemical Constants of Binary Systems, Vol. IV, p 40, Inter Science, New Yark, Values obtained by Interpollation from data by Akorlof (1932).

16 Scatchard, G., and Tefit, R.F., J. Amer. Chem. Soc. 52, 2271 (1930).

17 Evans,R.C. "An Introduction to Crystal Chemistry", 2nd Edn., Cambridge, at the University Press, P. 38, (1964).

18 Kressman, T.R.C. and Kitchner J.A., J. Chem., Soc., 1203, 1206 (1949).

19 Duncan, J.F. and Lister, B.A. Disc. Faraday Soc., 7, 104, (1949).

20 Bhatnagar, R.P. and Arora, R.C. J. Indian, Chem. Soc., 42, 640 (1965).

21 Lowen, W.K., Stoenner, R.W., Argersinger, W.J., Davidson, A.W. and Hume D.N. J. Am.Chem. Soc. 73, 2660 (1951).

22 Reichenberg D., Pepper, K.W. and Mecauley, D.J. J.Chem., Soc., Part I, 493 (1951).